

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

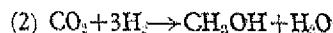
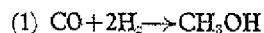
Process for Producing Methanol Synthesis Gas

We, METALLGESELLSCHAFT AKTIEN-GESELLSCHAFT, of 14, Reuterweg, Frankfurt-on-the-Main, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

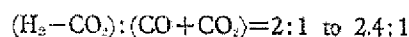
This invention relates to a process for producing methanol synthesis gas.

Recently, natural gas has been increasingly used as a starting material in the production of methanol synthesis gas, and sulphur-free natural gas is available for this purpose. Most of the natural gases which can be used in practice consist mainly of methane and owing to their C:H ratio cannot be used to produce a methanol synthesis gas by cracking with steam in a tube heater without a supply of extraneous carbon and/or elimination of surplus hydrogen, unless methanol is produced from an entirely non-stoichiometric mixture of carbon monoxide and hydrogen.

The following primary reactions take place during the production of methanol



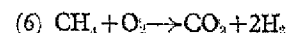
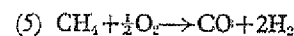
Thus, two moles of hydrogen are required for each mole of carbon monoxide and three moles of hydrogen for each mole of carbon dioxide. In synthesis gas for producing methanol, the H_2 :C mole ratio should be at least 2.0. In view of the proportion of carbon dioxide in the crude gas, a gas mixture is preferably used which meets the condition



In the cracking of methane with steam, three moles of hydrogen are formed for each mole of carbon monoxide and four moles of hydrogen for each mole of carbon dioxide by the reactions:



When methane is cracked with oxygen, 2 moles of hydrogen are formed per mole of methane by the reactions



When steam is used for cracking, the cracked gas thus contains a surplus of hydrogen whereas there is a surplus of carbon when oxygen is used as a cracking agent. The surplus carbon can easily be eliminated by scrubbing the cracked gas to remove carbon dioxide. The removal of hydrogen from a gas mixture is fairly difficult in practice and is uneconomical, even if the surplus hydrogen is used for other purposes.

For this reason, the reverse procedure is preferred in practice and there is an addition of extraneous carbon to the process of cracking methane with steam rather than a removal of hydrogen from the cracked gas. This carbon is usually added in the form of carbon dioxide, which may be taken from the surplus of other processes, e.g., from the production of ammonia synthesis gas, and is preferably recovered from the flue gases of the tube heater in which the methane is cracked. Because natural gas is suitably employed also as a fuel for heating the tube heater, the flue gas is free of sulphur.

5 In a number of chemical scrubbing processes for the recovery of carbon dioxide from flue gases, aqueous solutions of alkali metal carbonates or of alkali metal salts of weak organic acids, or organic bases, which may be in the form of an aqueous solution, are used as absorbents.

10 When carbon dioxide is scrubbed from flue gases with a solution of sodium carbonate or potassium carbonate, the scrubbing agent must be used at a high rate because it has only a small absorption capacity, and expensive equipment and a high consumption of steam and electric power are involved. When 15 absorbent solutions are used which have an alkaline reaction and contain organic components, such as alkylamines, alkanolamines or alkali metal salts of weak organic acids, the oxygen contained in the flue gas results in a considerable decomposition of the absorbent. This leads to considerable losses of scrubbing agent and a high risk of corrosion.

20 It has now been found that oxygen can be removed from the flue gas in an extremely simple and economic manner with means which are available in the plant itself so that the capital cost and operating cost involved in the scrubbing to remove carbon dioxide are much reduced.

25 According to the present invention there is provided a process for producing methanol synthesis gas, wherein a normally gaseous hydrocarbon is cracked with steam and carbon dioxide in a cracking furnace, and wherein 30 the carbon dioxide to be introduced into the cracking process is recovered from the flue gas of the cracking furnace when said flue gas has been treated to be free of oxygen, the carbon dioxide being introduced into the cracking process in an amount such as to provide an $H_2:C$ mole ratio of at least 2.

35 In one embodiment of the present process, the flue gas which is exhausted from the combustion chamber of the cracking furnace and has been cooled to temperatures between 100° and 450° C. in a waste heat boiler or mixture preheater contains about 1 to 5% oxygen and 40 is mixed within a so-called flue gas duct with a combustible gas and passed over a platinum-containing catalyst, which is provided in said flue gas duct. The oxygen contained in the flue gas is then consumed for the oxidation of the combustible gas which is supplied. The resulting temperature rise in the flue gas is utilized for an additional production of steam. The combustible gas consists preferably of a waste product of high-carbon content obtained in the production of methanol, e.g., a flashed-off gas from a methanol distillation plant, or dimethyl ether recovered from the distillation of crude methanol.

45 In general, the free oxygen which is still contained in the crude flue gas may be con-

sumed by a thermal or catalytic reaction with combustible gases which are admixed into the hot, crude flue gas, preferably with residual gases from the methanol synthesis and/or the distillation of the crude methanol, and the carbon dioxide is subsequently recovered from the flue gas in that the latter is scrubbed with an absorbent solution and said solution is regenerated. 70

75 The carbon dioxide recovered from the oxygen-free flue gas is added at such a rate to the gaseous hydrocarbons to be cracked that an $H_2:C$ mole ratio of 2:1 is obtained in the synthesis gas. For this purpose, it may be sufficient to use only a partial stream of the flue gas from the cracking furnace for a recovery of carbon dioxide after a removal of oxygen. 80

85 An important advantage of the present process resides in that the cracking furnace delivers directly a synthesis gas having the proper $H_2:C$ ratio. It is sufficient to cool said gas so as to remove steam as condensate and then to compress the gas before it can be used for synthesis. 90

95 Because the cracking furnace is generally heated with the gaseous hydrocarbons which are also the feed for the cracking process, the flue gas is free of sulphur. If the natural gas or the like which is available still contains sulphur, it may be desulphurized by known methods, e.g., by contact with zinc oxide.

100 In order to remove carbon dioxide from the flue gas which has been treated to be free of oxygen said gas may be scrubbed with an absorbent solution having an alkaline reaction, e.g., with an alkanolamine having a high absorption capacity. This practice will not involve a risk of a deterioration of the absorbent by oxidation nor an increased risk of corrosion. 105

110 Because the object of the scrubbing treatment to remove carbon dioxide is only to recover said carbon dioxide rather than to produce a scrubbed flue gas having a minimum residual concentration of carbon dioxide, an intense regeneration of the absorbent is not required. For this reason, the scrubbing plant for the recovery of carbon dioxide may be simple in design and comparatively small. 115

120 In order to enable the invention to be more readily understood, reference will now be made to the accompanying drawing which is a flow diagram representing by way of example a plant for carrying out the process according to the invention.

125 The plant shown in the drawing consists essentially of a tube heater 6, a scrubbing plant comprising an absorption tower or scrubber 45 and a regenerating tower 52, a steam boiler 32 with heaters 25 and 28 in a flue gas duct 24 of the tube heater, and an actual synthesis plant 15.

130 Pure methanol is delivered from the syn-

thesis plant at 16. The waste gases formed by the distillation of the crude methanol are passed through a conduit 26 to the flue gas duct, which contains a catalyst bed 27, in which the waste gases from the methanol distillation plant are oxidized with the residual oxygen in the flue gas.

The gas which has been withdrawn from the synthesis cycle is passed through a conduit 17 into a fuel conduit 18 leading to the tube heater to which combustion air is supplied by a compressor 20 through a conduit 21. A feed water supply conduit 33 leads to the steam boiler 32, and gaseous hydrocarbons to be cracked are introduced into the plant through a conduit 1.

The operation of the plant shown in the drawing will now be described in the following Examples of which Example 1 is in accordance with the invention and Example 2 is comparative.

EXAMPLE 1

Under a pressure of 11 kg./sq.cm. superatmospheric pressure, methane at a rate of 4000 standard cubic metres per hour from conduit 1 and carbon dioxide at a rate of 1100 standard cubic metres per hour from a conduit 58 are mixed and supplied to a preheater 2, in which the mixture of methane and carbon dioxide is heated to about 250° C.

When this mixture has left the preheater through a conduit 3, steam at a rate of 7000 kilograms per hour and under a pressure of 11 kg./sq.cm. superatmospheric pressure is added from a conduit 35 to the mixture. The mixture of methane, carbon dioxide and steam enters a heater 4, where it is heated to 450° C. and flows through a conduit 5 into the cracking tubes of the tube heater 6 where it is cracked with the application of extraneous heat and under a pressure of 7 kg./sq.cm. superatmospheric pressure and at a reaction temperature of 850° C. to produce a gas having the following approximate composition:

CO ₂	8.24% by volume
CO	20.85% by volume
H ₂	68.81% by volume
CH ₄	2.10% by volume

The cracked gas which has been formed at a rate of 16,500 standard cubic metres per hour contains steam at a rate of 4000 kilograms per hour. The mixture of cracked gas and steam flows through a conduit 7 to a cracked gas waste heat boiler 8, where it is cooled to about 480° C. by heat exchange with boiling water. From the boiler 8, the cracked gas flows to the heater 4 and from the latter through the conduit 7 to the preheater 2. The cracked gas flows subsequently through a conduit 10 into a cooler 11, where

the remaining residual heat which was not used for feed preheating in the heater 4 and in the preheater 2 is transferred to cooling water or air or feed water, and the steam contained in the cracked gas is condensed. The gas then flows through a conduit 12 to a compressor 13, in which it is compressed to about 320 kg./sq.cm. superatmospheric pressure, and is then fed through a conduit 14 to the methanol synthesis plant 15.

In the methanol synthesis plant, the reactants carbon dioxide, carbon monoxide and hydrogen are reacted in known manner to produce crude methanol, which is separated into its main constituents methanol, water and dimethyl ether in known manner by distillation.

Pure methanol at a rate of 6250 kilograms per hour, water at a rate of 1000 kilograms per hour and dimethyl ether at a rate of 72 kilograms per hour are produced from the cracked gas. From the gas cycle of the methanol synthesis gas, purge gas having the following composition:

CO ₂	1.0% by volume
CO	6.0% by volume
H ₂	75.0% by volume
CH ₄	18.0% by volume

is flashed off at a rate of 1000 standard cubic metres per hour.

When the crude methanol is flashed to the pressure of about 5 kg./sq.cm. superatmospheric pressure used in the distillation, and when the crude methanol is processed by distillation, gases having the following composition:—

CO ₂	26.0% by volume
CO	6.0% by volume
H ₂	36.0% by volume
CH ₄	32.0% by volume

are flashed off at a rate of 280 standard cubic metres per hour.

Whereas methanol leaves the plant through the conduit 16, the purge gas is supplied through the conduit 17 to the fuel gas conduit 18, where it is mixed with methane supplied at a rate of 1720 standard cubic metres per hour. The mixture is supplied to the burners 19 of the tube heater 6. Combustion air at a rate of 23,000 standard cubic metres is supplied to the burners 19 by the blower 20 in the conduit 21, an air preheater 22 and a succeeding conduit 23. The combustion produces flue gas having the following composition:

CO ₂	8.05% by volume
O ₂	1.73% by volume
N ₂	71.67% by volume
H ₂ O	18.55% by volume

at a rate of 25,600 standard cubic metres per hour.

The flue gas leaving the combustion chamber of the tube heater through the flue gas duct 24 is at a temperature of 970° C. and is cooled in a first waste heat boiler 25 to about 380° C. by heat exchange with boiling water. Flashed-off gas flowing at a rate of 280 standard cubic metres per hour from the methanol plant, and dimethyl ether at a rate of 72 kilograms per hour, are added to the flue gas flowing in the flue gas duct from the conduit 26. The resulting mixture is reacted with the oxygen contained in the flue gas in contact with a platinum-containing catalyst 27 disposed in the flue gas duct. The resulting combustion of the flashed-off gas and the dimethyl ether with consumption of the oxygen increases the flue gas rate to 25,780 standard cubic metres per hour and results in a gas of the following composition:—

	CO ₂	8.9% by volume
	N ₂	71.2% by volume
25	H ₂ O	19.9% by volume

The heat of combustion which is released increases the temperature of the flue gases to 600° C. In the second waste heat boiler 28, which is also contained in the flue gas duct, the flue gas is cooled to 380° C. by heat exchange with boiling water. The two waste heat boilers 25 and 28 as well as the cracked gas waste heat boiler 8 are connected by pairs of risers and downcomers 29, 30 and 31 to the steam drum 32, which is fed from a conduit 33 with preheated feed water and from which the resulting steam is withdrawn through a conduit 34. The steam is partly added through the conduit 35 to the mixture of methane and carbon dioxide and is partly supplied through a conduit 36 to other consumers, such as the methanol distilling unit and the regenerator of the scrubbing stage for the carbon dioxide removal.

The flue gas flows also through the air preheater 22, where it is cooled to about 150° C. whereas the combustion air is heated at the same time to 325° C. From the air preheater 22, the flue gas flows through a conduit 37 to a flue gas blower 38, which maintains the desired subatmospheric pressure in the combustion chamber of the tube heater. From the flue gas produced at a rate of 25,780 standard cubic metres per hour, 13,080 standard cubic metres per hour are discharged without further cooling into the atmosphere through a conduit 39. The remainder amounting to 12,700 standard cubic metres per hour is supplied through a conduit 40 to a cooler 41, where the steam contained in the flue gas is condensed and the flue gas is cooled to about 40° C. The flue gas remaining after the removal of steam amounts

to 10,200 standard cubic metres per hour and has the following composition:

CO ₂	11.1% by volume
N ₂	88.9% by volume

This flue gas is supplied through a conduit 42 to a blower 43, where the pressure of the gas is increased by about 900 millimetres water. The compressed gas is introduced by a conduit 44 into the scrubber 45.

In this scrubber, carbon dioxide is removed from the flue gas to a residual content of about 2% by treatment with an absorbent alkaline solution which trickles down the scrubber. Carbon dioxide at a rate of 1100 standard cubic metres per hour is absorbed by the absorbent solution. The remainder, consisting of 22 standard cubic metres CO₂ per hour together with 9,078 standard cubic metres nitrogen per hour, is discharged through a conduit 47 is fed by a pump 48 through a conduit 49 to a heat exchanger 50, where the solution is heated. From the heat exchanger 50, the solution flows through a conduit 51 to the upper portion of the regenerator 52 and trickles through the latter from top to bottom. A steam-heated reboiler 53 connected to the lower portion of the regenerator causes the absorbent solution to boil.

The rising steam causes a release of the carbon dioxide which has been absorbed by the alkaline solution in the scrubber. The released carbon dioxide at a rate of 1100 standard cubic metres per hour and the steam which is not condensed in the regenerator flow together through a conduit 54 to a cooler 55, where they are cooled and the steam is condensed. From the cooler, the carbon dioxide, which is under a slight superatmospheric pressure of about 100 to 500 millimetres water is passed through a conduit 56 to a compressor 57, where it is compressed to 11 kg.sq./cm. superatmospheric pressure and then flows through the conduit 58 into the conduit 1, where it is mixed with the feed gas.

The absorbent solution which drains from the regenerator through a conduit 59 and has been freed to a high degree from carbon dioxide is fed by a pump 60 through a conduit 61 to the heat exchanger 50, where it is precooled, by a heat exchange with the "laden" solution. The regenerated solution then flows through a conduit 62 to a cooler 63, where it is cooled to the scrubbing temperature of about 45° C., and thereafter through a conduit 64 into the scrubber.

EXAMPLE 2

In this Example, the plant and the operation thereof are substantially the same described in Example 1, with the exception that the platinum-containing catalyst 27 is omitted. Flashed-off gas discharged at a rate of 280 standard cubic metres per hour by the meth-

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anol distillation plant, and dimethyl ether at a rate of 75 kilograms per hour, are burnt with the aid of air, which is supplied to the combustion chamber at a rate of 2180 standard cubic metres per hour by aspirating burners. When the process is controlled in the same manner in other respects, the rate of flue gas increases from 25,600 standard cubic metres per hour to 28,070 standard cubic metres per hour and the temperature of the flue gas rises to 525° C. The flue gas contains oxygen and has the following composition:—

CO ₂	8.2% by volume
O ₂	1.7% by volume
N ₂	71.8% by volume
H ₂ O	18.3% by volume

Just as in Example 1, this flue gas is cooled to about 150° C. by a transfer of heat to boiling water in the waste heat boiler 28 and to the combustion air in the air preheater 22 and flows through the conduit 37 to the flue gas blower 38.

Of the flue gas stream of 28,070 standard cubic metres per hour, a stream of 14,320 standard cubic metres per hour is discharged through the conduit 39 to the atmosphere. The remainder, consisting of 13,750 standard cubic metres per hour, flows through the conduit 40 to the cooler 41, where the flue gas is cooled and the steam contained therein is condensed. When the steam has been separated, the remaining flue gas stream of 11,240 standard cubic metres per hour has the following composition:

CO ₂	10.0% by volume
O ₂	2.1% by volume
N ₂	87.9% by volume

and flows through the conduit 42 to the blower 43, where the pressure of the flue gas is increased by 900 millimetres water. The flue gas flows subsequently through the conduit 44 into the scrubber 45, where the absorbent solution trickling down absorbs carbon dioxide at a rate of 1100 standard cubic metres per hour. The remaining gas flows through the conduit 46 to the atmosphere. The solvent cycle regeneration and recirculation of carbon dioxide to the feed gas in the conduit 1 are as described in Example 1.

In both examples, the absorbent consisted of an aqueous solution of alkali metal salts of simple amino acids ("Alkazid").

The oxygen-containing flue gas of Example 2 caused changes of the absorbent by oxida-

tion resulting in a loss of 3.5 kilograms absorbent per hour, and required a corrosion-resisting carbon dioxide recovery plant.

Also, the waste heat boilers contained in the flue gas duct produce about 30% less steam than in Example 1, the carbon dioxide partial pressure in the flue gas is lower by 11% and, consequently, the circulation of absorbent in the carbon dioxide recovery plant is higher by 11% so that the power requirement of the compressors and pumps is increased. From the above, it can be calculated that the low concentration of oxygen in the flue gas involves an increase in operating cost by about £2 12s. 0d. per hour. This corresponds to about £21,000 in 8,000 stream hours during one year.

WHAT WE CLAIM IS:—

1. A process for producing methanol synthesis gas, wherein a normally gaseous hydrocarbon is cracked with steam and carbon dioxide in a cracking furnace, and wherein the carbon dioxide to be introduced into the cracking process is recovered from the flue gas of the cracking furnace when said flue gas has been treated to be free of oxygen, the carbon dioxide being introduced into the co-acting process in an amount such as to provide an H₂:C mole ratio of at least 2.

2. A process as claimed in Claim 1, wherein a reaction between the free oxygen contained in the crude flue gas and combustible gases or vapours introduced into the same is induced thermally or by catalysts which contain platinum or another platinum group metal.

3. A process as claimed in Claim 2, wherein combustible gases which are introduced into the crude flue gas for reaction with the oxygen comprise residual gases of high-carbon content from the synthesis of methanol and/or a succeeding distillation of methanol.

4. A process according to Claim 2 or 3, wherein a combustible vapour which is introduced into the crude flue gas comprises dimethyl ether, which is formed in the synthesis of methanol and recovered by a succeeding distillation of methanol.

5. A process as claimed in any one of Claims 1 to 4, wherein carbon dioxide is recovered from the flue gas by scrubbing the flue gas with an organic base or an aqueous solution of an organic base or of an alkali metal salt of a weak organic acid.

6. A process as claimed in any one of Claims 1 to 5, wherein a partial stream of the flue gas exhausted from the cracking furnace is treated to be free of oxygen and is processed to recover carbon dioxide.

7. A process for producing methanol synthesis gas substantially as hereinbefore described with reference to the accompanying drawing and/or in Example of the foregoing
- 5 Examples.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*